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(54) Title: DRILLING FLUID ADDITIVES FOR IMPROVED SHALE STABILIZATION, THE DRILLING FLUID FORMED THEREFROM AND METHOD OF USING SAME

(57) Abstract

A drilling fluid additive for use with water sensitive shales, clay or fines is presented which comprises a water soluble polymer, such as for example, polyvinylpyrrolidone, polyvinylalcohol, polysaccharides, or partially hydrolyzed polyacrylamide in combination with a sulphosuccinate surfactant, an acetylenic alcohol surfactant or a surfactant made from the sodium salts of sulfonated naphthalene-formaldehyde condensates.

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DRILLING FLUID ADDITIVES FOR IMPROVED SHALE STABILIZATION, THE DRILLING FLUID FORMED THEREFROM AND METHOD OF USING SAME

Summary of the Invention:

The above-discussed and other problems and deficiencies of the prior art are overcome or alleviated by method and composition for providing enhanced shale stabilization of the present invention. In accordance with the present invention, an additive for water based drilling fluids comprises a water soluble polymer such as polyvinylpyrrolidone (PVP) and copolymers such as vinylpyrrolidone-codimethylamino ethyl methacrylate, polyvinylalcohol (PVA), partially hydrolyzed polyacrylamide (PHPA), and/or polysaccharides combined with surfactants selected from the group of sulphosuccinates, acetylenic alcohols and sodium salts of sulfonated naphthalene formaldehyde condensates.

In accordance with another embodiment of the present invention there is provided a well fluid comprising an aqueous component and including the well fluid additive described above.

In accordance with still another embodiment of the present invention there is provided a method of stabilizing a subterranean formation penetrated by a borehole and having water sensitive shales, clays or fines. The method generally includes introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid comprises the well fluid additive described above.

The water-based drilling fluids treated with this class of surfactants exhibit stable rheological and filtration control properties, particularly after exposure to high temperatures (e.g., 250°F).

Particularly preferred polymer/surfactant systems include the polysaccharide/sulphosuccinate or acetylenic alcohol combination which has the advantage of being nontoxic and biodegradable. The PVP/sulphosuccinate combination shows excellent tolerance for solids.

Optionally, in the above embodiments, the well fluid additive, the well fluid, and the treatment fluid utilized in the above method, can all further contain a glycol which, together with the water-soluble polymer and surfactant, can provide a

synergistic effect.

The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description.

Field of the Invention:

This invention relates to a drilling fluid composition and method of drilling a subterranean well to inhibit the absorption of aqueous medium by shales in aqueous alkaline environments. More particularly, this invention relates to a method and composition for reducing shale swelling where the shale is stabilized using certain surfactants including sodium salts of sulfonated naphthalene-formaldehyde condensates, sulphosuccinates and acetylenic alcohol surfactants which are added to water-based drilling fluids prepared with certain polymers such as polyvinyl pyrrolidone, polyvinylalcohol, particularly hydrolyzed polyacrylamide and polysaccharides.

Background of the Invention:

A rotary system is a common form of drilling a subterranean well. This system depends upon the rotation of a column of drill pipe to the bottom to which is attached a multi-prong drilling bit. The drill bit cuts into the earth, causing cuttings. A drilling fluid must be used to carry these cuttings to the surface for removal to allow the bit to continue functioning and the bottom of the hole to be kept clean and free of cuttings.

Aqueous based drilling fluids are frequently utilized in the drilling, completion and workover operations of subterranean wells. Such drilling fluids utilize clear water, brine, or sea water as the primary liquid phase, to which may be added known dispersants or deflocculants, filtration control agents, viscosifiers and suspending and weighting agents, such as bentonite and barite, respectively.

In most areas, the major portions of the formations penetrated while drilling a well are shale. By shale it is meant materials such as bentonite and the like, claystones and gumbo-type colloidal-clay substances and related substances which possess the property of hydrodynamic volume increase when exposed to aqueous environments. These water sensitive shales hydrate in water rather easily and may

swell to many times their original size. Swelling herein refers to the hydrodynamic volume increase of the shale.

Swelling of shales is believed to be attributable to surface hydration, interlayer swelling and osmotic swelling. Surface hydration is adsorption of water onto the shale surfaces and is particularly active in shales because of high surface area. Shales, particularly smectites, may have a lattice-type structure which allows the water to be adsorbed between layers as well as upon the particle surface. This absorbed water is considered held by hydrogen bonding to basal surfaces which, because of atomic structure normally have a net negative charge. On the other hand, osmotic swelling occurs because the concentration of cations adsorbed on the basal surface of the clays and held at surface edges is greater than in the liquid itself. This force draws the liquid into the shale particle. Of course, the degree of the osmotic effect depends on the salt concentrations both in the shale particle and in the liquid.

Drilling of water sensitive shales with conventional water-base drilling fluids has long been plagued with problems. The shale formation penetrated may swell and slough as a result of interaction with the drilling fluid, and cave in, leading to hole enlargement and serious mechanical difficulties. Further, interaction between water and water sensitive shale usually has an adverse effect on drilling fluids, because the shale disperses into colloidal sized particles of clay which tend to increase the viscosity and density of the drilling fluids to such an extent that they are unusable without considerable dilution and chemical treatment. These difficulties have led to efforts to inhibit shale swelling during drilling. Inhibition of swelling herein means the ability of a process to retard the hydration of shales so they remain substantially cohered and basically substantially in their original size, shape and volume.

One early method of inhibiting the swelling of shale when drilling subterranean wells with a water base drilling fluid was the use of calcium-treated muds. The polyvalent calcium cation holds the clay layers in together, it is thought, by bonding to the layer surfaces in competition with water molecules. Calcium is provided by lime hydrate, gypsum and calcium chloride, and occurs in sea water. Calcium treated muds and sea water require thinners such as lignosulfonate, because the divalent calcium cation is flocculating. However, in deep hot holes, calcium treated muds tend to setup or become so highly gelled they cannot be circulated out.

The so-called polymer muds have come into later favor, generally relying on a

combination of polymers and soluble salts to inhibit swelling and dispersion. Commonly used polymers are cellulose derivatives, partially hydrolyzed polyacrylamide ("PHPA"), xanthan gum and biopolymers, e.g., so-called X-C polymers (when identified by the bacteria which produce it by action on carbohydrates). The commonly used polymers are anionic polyelectrolytes and are thought to be adsorbed at positive charge sites on the edges of layer surfaces at multiple places along the chain length of the polymer, thereby binding the clay particles together and encapsulating cuttings. Soluble salts are needed in these muds to provide cations to react with the net negatively charged layer surfaces and thereby reduce the repulsing forces between clay surfaces. Potassium salts (potassium chloride is the usual salt preferred) are considered more effective at repressing swelling and dispersion than sodium salts. For example, see U.S. Patents 3,738,437 and 4,664,818. However, these polymer mud systems are now less available. Environmental regulations restricting release of chlorides into on-shore waters are increasingly limiting use of alkali metal chlorides to offshore drilling muds, where chlorides release into naturally salty sea water is not restricted.

While the foregoing polymer-based mud systems are now frequently used in rotary drilling operations, such mud systems, including those based on PHPA suffer from certain disadvantages. For example, such polymer-based drilling fluids can exhibit (1) poor tolerance for solids contamination; (2) degradation and reduction in performance at high temperature conditions (e.g., bottom hole temperatures); and (3) polymer hydrolysis and associated poor performance at high pH and high salt concentrations.

<u>Description of the Preferred Embodiment:</u>

This invention presents a shale swelling inhibitor (e.g., stabilizing composition) comprising a well fluid additive which includes at least one surfactant selected from the group of sulphosuccinates, acetylenic alcohols and sodium salts of sulfonated naphthalene- formaldehyde condensates combined with a water soluble polymer. This well fluid additive finds utility in a broad range of well fluids in which it is desirable to stabilize water-sensitive shales, clays and other fines.

In the practice of the drilling method of the present invention, the drillstring is rotated to cut a borehole into the earth while circulating a drilling fluid down through

the drillstring and then up the annulus between the drilling string and the wall of the borehole. The drilling fluid utilized in the drilling method of the present invention will comprise an aqueous component and the above described additive of the present invention.

The aqueous medium employed in the well fluids of the present invention may be any kind of water from any source including, but not limited to, fresh water, sea water, water from the subterranean reservoir, or a natural or synthetic brine; although as discussed in the examples, certain of the surfactants perform better in salt water (as opposed to fresh water).

Polymers suitable to be utilized in the present invention will generally be water soluble. The polymers of the present invention preferably also have good wetting properties and a reasonable rate of dissolution in water for convenient use in the field. They should also afford aqueous solutions of low to moderate viscosities as are traditionally used in drilling wells, particularly oil and gas wells. Additionally, it is preferable that the polymer be capable of encapsulating the water-sensitive shale, clay or other fines. It is also preferable that the polymer have suitable thermal stability for the environment in which the well fluids are employed. This generally means thermal stability up to and exceeding 250°F. It is also preferable that the polymer have suitable resistance to hydrolysis under high pH, generally in the range of about 9 to about 11. Where necessary to achieve proper water solubility and other suitable properties, the polymers of the present invention may be hydrolyzed. For example, polyvinylalcohol will generally be eighty five percent or more hydrolyzed. Finally, it is also preferred that the polymers of the present invention have good tolerance to drilled solids contamination.

Examples of polymers suitable for use in the present invention include polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides. Derivatized starches such as substituted and non-substituted alkyl starches, especially hydroxy propyl starches may be utilized as the polymer in the practice of the present invention.

The polyvinylpyrrolidone utilized in the present invention may be prepared by any suitable method known to those of skill in the art. The average molecular weight of the polyvinylpyrrolidone must be suitable for effective encapsulation of the drill

cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. Generally, the average molecular weight of the polyvinylpyrrolidone utilized in the present invention will be at least 1000, preferably in the range of about 10,000 to about 1,500,000, more preferably in the range of about 500,000 to about 1,200,000, and most preferably in the range of about 750,000 to about 1,000,000. Examples of polyvinylpyrrolidone copolymers include a copolymer of vinylpryyolidone and styrene. Another vinyl pyrrolidone copolymer is the dimethylamino ethyl methacrylate and vinylpyrrolidone.

The polyvinylalcohol of the present invention may be prepared by any suitable method known to those of skill in the art. The molecular weight of the polyvinylalcohol must be suitable for effective encapsulation of the drill cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. Generally, the average molecular weight of the polyvinylalcohol utilized in the present invention will be at least 50,000, preferably in the range of about 50,000 to about 200,000 more preferably in the range of about 100,000 to about 175,000 and most preferably in the range of about 125,000 to about 175,000. Polyvinylalcohols suitable for use in the present invention will have a percent hydrolysis of at least 60 percent, and preferably in the range of about 80 to about 99 percent. Polyvinylalcohol may be utilized in solid or solution form.

The partially hydrolyzed polyacrylamides useful in the practice of the present invention may be obtained by any suitable method known to those of skill in the art. One suitable method generally involves polymerizing and subsequently hydrolyzing acrylamide (or a lower homolog of acrylamide) or copolymerizing acrylamide with an acrylate, or the like. The range of hydrolysis (and/or the proportion of the amide groups of the polyacrylamide that are carboxyl groups or have been hydrolyzed to form carboxyl groups) should be greater than about 20 percent. Preferably, the partially hydrolyzed polyacrylamide polymer will have a percent hydrolysis in the range of about 30 to about 50 percent. The molecular weight of the partially hydrolyzed polyacrylamide will be in the range of about 500,000 to about 20,000,000.

The term "partially hydrolyzed polyacrylamide" will generally include polyacrylamides as well as copolymers of acrylamide with other suitable monomers

and polymers. Examples of other suitable polymers useful as partially hydrolyzed polyacrylamides includes partially hydrolyzed acrylamide/acrylate copolymers, partially hydrolyzed acrylamide/acrylic acid copolymers, partially hydrolyzed acrylamide/styrene sulfonic acid copolymers, partially hydrolyzed acrylamide/acrylamide propane sulfonic acid copolymer (AMPS), a copolymer of acrylamide and vinylpyrrolidone, and a copolymer of acrylamide, acrylate and vinylpyrrolidone.

In the practice of the present invention, when a water soluble component is utilized, the well fluid additive will generally comprise in the range of about 1 to about 99 volume percent water soluble component. Preferably, the well fluid additive will comprise in the range of about 5 to about 90 volume percent water soluble component. More preferably, the well fluid additive will comprise in the range of about 10 to about 80 volume percent, and most preferably in the range of about 30 to about 70 volume percent non-water soluble component.

The surfactant utilized in the practice of the present invention is selected from the classes of surfactants known as (1) sulphosuccinates, (2) acetylenic alcohols and (3) sodium salts of sulfonated naphthalene-formaldehyde condensates. Suitable commercially available sulphosuccinates include Air Products Aerosol® IB-45. Suitable commercially available acetylenic alcohols include Air Products Surfynol® 502 and 504. Suitable commercially available sodium salts of sulfonated naphthalene-formaldehyde condensates include Rhone-Poulene Rhodacal®N.

The relative amounts of the components of the well fluid additive of the present invention are generally selected to provide compatibility with each other and with the well fluid, and to provide suitable shale, clay or fines stabilization.

Generally based on the total weight of the well fluid additive, the well fluid additive of the present invention will comprise in the range of about 0.1 to about 50% weight percent polymer and in the range of about 1 to about 50% weight percent surfactant. Preferably, the well fluid comprises in the range of about 0.1 to about 2 weight percent polymer, and in the range of about 1.5 to about 2.5 weight percent surfactant, and most preferably in the range of about 0.5 to about 1 weight percent polymer, and in the range of about 1 to about 2 weight percent surfactant.

In the practice of the present invention, the well fluid additive is generally added to the well fluid in an amount in the range of about 3 to about 70 pounds/bbl

well fluid.

Polyglycols suitable for use in the present invention generally have a molecular weight that will render the polyglycol sufficiently water soluble or poorly water insoluble and of proper viscosity so as not to inhibit preparation and handling. Generally for most polyglycols, this means a molecular weight in the range of about 100 to 1200. Accordingly, it is believed that for most polyglycols, a molecular weight above about 1200 will have a tendency to be water insoluble or at least not sufficiently water soluble for use in the present invention. Of course, in those instances where a certain polyglycol may have a molecular weight outside of the above range and still be suitable, it may certainly be utilized.

Polypropylene glycols having a molecular weight in the range of about 200 to about 600 are most preferred for use as the alcohol component of the present invention.

Generally, the glycols will be added in the range of about 1 to about 10 weight percent.

It is also to be understood that other additives used by those skilled in the art may also be added to the drilling fluids of the present invention, as long as they do not have a substantial detrimental effect on the well fluid, including but not limited to, for example, other surfactants, weighting materials, breakers, loss circulation additives and salts.

EXAMPLES

Table 1 below is a example of an aqueous "control" drilling fluid which contains no water soluble polymer or surfactant. It should be noted that the % erosion loss is 65.4. Biozan is Whelan Gum. MIL-PAC LV is a low viscosity polyanionic cellulose useful as a filtration control agent and MIL-BAR is barite useful as a weighting agent, both of which are available from Baker Hughes Inteq. Biozan is available from Kelco.

TABLE 1

	Control
Materials:	
Seawater	0.86
Caustic soda, lb	0.5
MIL-PAC LV, lb	2.0
Biozan, lb	0.75
MIL-BAR, lb	204
Rolled 4 hr. at 150°F	
Add 25 g HOLE-PLUG to each mud sample	
Rolled 16 hr at 250°F	
Sieve mud sample with 18-mesh screen	
<u>Properties</u>:	
Apparent Viscosity, cp	27.5
Plastic Viscosity, cp	16
Yield Point, lb/100 sq ft	23
10-sec Gel, lb/100 sq ft	6
10-min Gel, lb/100 sq ft	7
API Fluid Loss, ml	96
HOLE-PLUG, g (after wash & dry)	7.9
% Erosion Loss (calculated on basis of initial 8.8% moisture content)	65.4

<u>Examples 1-39</u>

The following examples show the favorable use of water soluble polymers and sulphosuccinate surfactants.

Materials

The poly(vinyl pyrrolidone) used was Luviskol K-90 (average molecular weight = 1,000,000 g/mol) from BASF. The initial poly(vinyl alcohol) used was a 75% hydrolyzed sample (PHPVOH) from MTM Research. The commercial poly(vinyl alcohol) sample used was Airvol 540S from Air Products (88% hydrolyzed and with a molecular weight of 100,000 g/mol). The partially hydrolyzed polyacrylamide used were Baker Hughes Inteq products (New Drill, HP and New Drill, Plus). The sulfosuccinates studied were Aerosol IB-45 and Aerosol OS from American Cyanamid.

Equipment

All laboratory barrels of fluid were mixed in a MULTIMIXER for a total of 45 minutes. The API's were measured in an API filtration apparatus. Rheological properties were measured at room temperature with a FANN 35 VISCOMETER. All rolling erosion studies were carried out in steel cells. All solids contamination studies were carried out in pint jars. Capillary section time (CST) tests were done in a CST instrument.

Samples

Initial evaluation of polymer/surfactant systems were done by using Volclay pellets and allowing the pellets to soak in a beaker containing the polymer/surfactant solution overnight. The evaluation in these cases was qualitative. After the best combination had been obtained, a quantitative estimate of the performance was done by doing rolling erosion tests. These polymer/surfactant systems were tested in both sea and fresh water. The specific components and ratio of components used to prepare the muds are described on tables 2-8. Rolling erosion tests were done by adding 25 grams of hole plug (3/8" size from Bariod Corporation) to each steel cell

containing the mud system prepared, then, placing the cell in an oven with rollers and allowed to roll at 250°F for 16 hours. After this time, the mud was filtered with a mesh and the non-reactive shale was then rinsed with water and dried at 250°F for four hours prior to weighting. The properties of the mud were then measured.

Discussion of Examples 1-39

The addition of a sulfosuccinate to a partially hydrolyzed polyacrylamide (New Drill Plus) sea water mud improves the shale stability by 40% (51% erosion without surfactant vs 30% with surfactant) while keeping good API filtrate values and rheological properties (Table 2). In this case, the Aerosol OS performs about the same as the Aerosol IB-45 (29 and 31% erosion, respectively). In the case of a fresh water mud containing the Aerosol IB-45 and PHPA (New Drill Plus) the improvement on the shale stability is more dramatic (97% erosion without surfactant vs 10% erosion with surfactant), while keeping the API filtrate low (2.8 ml).

According to the data reported on Table 3, the addition of sulfosuccinates to poly(vinyl pyrrolidone) in sea water does not improve the shale stability, but this data reveals that poly(vinyl pyrrolidone) by itself improves the shale stability (% erosion after 16 hours at 250°F is 90%). In addition, in fresh water there is also no improvement in shale stability by adding sulfosuccinates.

The poly(vinyl alcohol)/sulfosuccinate system (Table 4) revealed that in sea water poly(vinyl alcohol) improves the shale stability (% erosion = 20 after 16 hrs at 250°F). When a sulfosuccinate is added to the poly(vinyl alcohol) mud system further improvement (35%) in the shale stability is obtained (20% erosion without surfactant vs 13 and 7% erosion with surfactant). In this case, there is a distinct difference between the Aerosol OS and the Aerosol IB-45. The OS performs better, but the interaction of this surfactant with the polymer leads to polymer precipitation

from the mud, therefore the IB-45 is preferred. It can also be seen from Table 3 that the API filtrate is reduced by 40-50% when the sulfosuccinate is added to this polymer system.

On the other hand, in a fresh water mud, poly(vinyl alcohol) by itself and with addition of sulfosuccinate do not improve the shale stability (% erosion 90-93%). One of the advantages of poly(vinyl alcohol) is the fact that it has good thermal stability and good stability under alkaline pH compared to partially hydrolyzed polyacrylamide which hydrolyzes at high pH.

Capillary Section Time Results

According to the results reported on Table 5 the largest interaction between the surfactant and the clay occurs at a 2% surfactant concentration for the Aerosol IB-45. A concentration of 2% per barrel was the amount used while evaluating this surfactant with different polymers. In the case of Aerosol OS, the major interaction with the clay occurs at 1% concentration of surfactant.

Toxicity and biodegradation

Aerosol IB-45 underwent a 48 hour range finding test using the UK protocol for toxicity testing of drilling fluid chemicals. The results from this range finding test indicates an LC 50 of 500-1000 ppm. Biodegradation studies using the 28 day closed bottle method was done on the Aerosol IB-45. The results from this test revealed that the IB-45 degraded 40% under this condition.

Poly(vinyl alcohol) is a relatively low toxic material used in food packaging Poly(vinyl alcohol) was submitted for biodegradation studies using the 28 day closed bottle method. Results from this test revealed that poly(vinyl alcohol) degraded 37.13% after 28 days. NEW DRILL PLUS was also submitted to the 28 day bottle biodegradation test. The results revealed that NEW DRILL PLUS degraded by 16%

after 28 days.

According to the biodegradation and toxicity data, it can be concluded that the use of poly(vinyl alcohol) is a considerable improvement over PHPA in terms of biodegradation. In addition, the use of IB-45 in conjunction with PHPA will not add to the toxicity or decrease biodegradation but, on the contrary, it may improve the final results.

Effects of Solids Contamination

The effect of solids contamination on the rheological properties of muds prepared with poly(vinyl alcohol)/sulfosuccinates in sea water are reported on Table 6. As can be seen from this data, this system showed very good tolerance for solids since there is very little change in the rheological properties as the amount of solids increases. The NEW DRILL PLUS/sulfosuccinates system (Table 8) showed some improvement over the solids contamination compared to NEW DRILL PLUS by itself. The Poly(vinyl pyrrolidone)/sulfosuccinate system (Table 7) showed very good tolerance for solids.

Conclusions

Based on the data presented in this report, stable-water polymer muds can be made with poly(vinyl alcohol) and PHPA. The addition of a surfactant such as Aerosol IB-45 improved the shale stabilizing power of the PHPA in sea and fresh water (40% and 90%, respectively). Addition of the same surfactant to poly(vinyl alcohol) gave considerable improvement to shale stability in sea water only.

New Drill Plus and Sulfosuccinates Muds in Fresh and Sea Water

Sample	1	2	3	4	5
Water, ml	300	300	300	300	300
Sea Salt, g	13	13	13	-	-
New Drill, g	2	2	2	2	2
Caustic, g	0.5	0.5	0.5	0.2	0.2
Milpac LV,g	2	2	2	2	2
Biozan, g	0.75	0.75	0.75	0.75	0.75
Surfactant	-	Aerosol OS 3.5 g	Aerosol IB-45 7 ml	-	Aerosol IB-45 7 ml
Barite, g	204	204	204	204	204

Rheological Properties of Muds After Dynamic Aging at 250°F for 16 Hours

Sample	1	2	3	4	5
θ 600	78	110	118	100	*
θ 300	52	75	80	56	218
PV	26	35	38	44	-
YP	26	40	42	12	-
API, ml	3.4	2.8	2.6	6.5	2.8
% Erosion	51	29	31	97	10

* Off Scale

TABLE 3
Poly(vinyl pyrrolidone) and Sulfosuccinates Muds in Fresh and Sea Water

Sample	6	7	8	9	10
Water, ml	300	300	300	300	300
Sea Salt, g	13	13	13	-	-
K-90, g	2	2	2	2	2
Caustic, g	0.5	0.5	0.5	0.2	0.2
Milpac LV, g	2	2	2	2	2
Biozan, g	0.75	0.75	0.75	0.75	0.75
Surfactant	-	Aerosol OS 3.5 g	Aerosol IB-45, 7 ml	-	Aerosol IB-45, 7 ml
Barite, g	204	204	204	204	204

Rheological Properties of Muds after Dynamic Aging at 250°F for 16 Hours

Sample	6	7	8	9	10
600	66	82	69	172	*
300	44	52	44	114	225
PV	22	30	25	58	-
YP	22	22	19	56	-
API, ml	7.8	7.0	7.0	10	12
% Erosion	9.2	24	15	93	95

* Off Scale

TABLE 4

Poly(vinyl alcohol) and Sulfosuccinates Muds in Fresh and Sea Water

Sample	11	12	13	14	15	16
Water, ml	300	300	300	300	300	300
Sea Salt, g	13	13	13	-	-	-
Caustic, g	0.5	0.5	0.5	0.2	0.2	0.2
Airvol 540S, g	2	2	2	2	2	2
Milpac LV, g	2	2	2	2	2	2
Biozan, g	0.75	0.75	0.75	0.75	0.75	0.75
Surfactant	-	Aerosol IB 45, 7 ml	Aerosol OS, 3.5 g	-	Aerosol IB-45, 7 ml	Aerosol OS, 3.5, g
Barite, g	204	204	204	204	204	204

Rheological Properties of Muds After Dynamic Aging at 250°F for 16 Hours

Sample	11	12	13	14	15	16
600	49	68	80	184	*	*
300	33	44	55	125	243	245
PV	16	24	25	59	-	-
YP	17	20	30	66	-	-
API, ml	11	7	5	11	N/C	9
% Erosion	20	13	7	94	90	93

* Off Scale

TABLE 5
Capillary Section Time (CST) Evaluation of Sulfosuccinates

Sample	17	18	19	20	21	22	23	24
Milgel, g	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water, ml	20	20	20	20	20	20	20	20
Surfac-tant %	-	Aerosol OS 0.5	Aerosol OS 1.0	Aerosol OS 2.0	Aerosol OS 2.5	Aerosol IB-45 0.5	Aerosol IB-45 1.0	Aerosol IB-45 2.0

Readings on the CST Instrument for Muds Described Above

Sample	17	18	19	20	21	22	23	24
Readings Sec	237	265	225	356	324	319	299	149

TABLE 6

Effects of Solids on the Rheological Properties of the Poly(vinyl alcohol)/Sulfosuccinates System in Sea Water

Sample	25	26	27	28	29
Water, ml	300	300	300	300	300
Sea Salt, g	13	13	13	13	13
Caustic, g	0.5	0.5	0.5	0.5	0.5
Airvol 540S, g	2	2	2	2	2
Biolose, g	2	2	2	2	2
XC Polymer, g	0.75	0.75	0.75	0.75	0.75
Aerosol IB-45, ml	-	7	7	7	7
Barite, g	50	50	50	50	50
Rev-Dust, g	0	20	40	60	80

Rheological Properties of Muds after Dynamic Aging at 150°F for 16 Hours

Sample	25	26	27	28	29
600	23	22	33	38	45
300	15	13	21	25	30
PV	8	9	12	13	15
YP	7	4	9	12	15
10-S	2	2	3	2	3
10-M	1	2	2.5	3	4
API, ml	3.6	3.8	6.4	8	13

TABLE 7

Effect of Solids on the Rheological Properties of the Poly(vinyl pyrrolidone)/Sulfosuccinates System in Sea Water

Sample	30	31	32	33	34
Water, ml	300	300	300	300	300
Sea salt, g	13	13	13	13	13
Caustic, g	0.5	0.5	0.5	0.5	0.5
Airvol 540S, g	2	2	2	2	2
Biolose, g	2	2	2	2	-
XC Polymer, g	0.75	0.75	0.75	0.75	0.75
Aerosol IB-45, ml	-	7	7	7	7
Barite, g	50	50	50	50	50
Rev-Dust, g	0	20	40	60	80

Rheological Properties of Muds after Dynamic Aging at 150°F for 16 Hours

Sample	30	31	32	33	34
600	22	22	28	32	44
300	16	14	19	22	30
PV	6	8	92	10	14
YP	10	6	10	12	16
10-S	2	3	2	3	4
10-M	2	3	3	3	5
API, ml	5.6	5.8	5.8	7.4	7.4

TABLE 8

Effects of Solids Contamination on the Rheological Properties of NEW DRILL PLUS/Sulfosuccinate System in Sea Water

Sample	35	36	37	38	39
Water, ml	300	300	300	300	300
Sea salt, g	13	13	13	13	13
Caustic, g	0.5	0.5	0.5	0.5	0.5
New Drill Plus	2	2	2	2	2
Biolose, g	2	2	2	2	-
XC Polymer, g	0.75	0.75	0.75	0.75	0.75
Aerosol IB-45, ml	-	7	7	7	7
Barite, g	50	50	50	50	50
Rev-Dust, g	0	20	40	60	80

Rheological Properties of Muds after Dynamic Aging at 150°F for 16 Hours

Sample	35	36	37	38	39
θ600	68	70	84	113	134
θ300	48	50	61	85	100
PV	20	20	23	28	34
YP	28	30	38	57	66
10-S	5	6	9	11	14
10-M	4.5	5	9	11	14
API, ml	3.4	4.8	4.8	5.0	4.4

Examples 40-45

Materials

The poly(vinyl alcohol) used in these examples was obtained from Air Products under the trade name of Airvol 540S. This polymer has an average molecular weight of 100,000 g/mol. Surfynol 502 and 504 are acetylenic alcohol surfactants commercially available from Air Products. Milpac LV and Mil-Bar are Baker Hughes Inteq products. Biozan is commercially available from Kelco. Muds were prepared using a multimixer. The additives used and the amount of each are reported on Table 9. To each mud sample, 25 grams of Hole-Plug were added. The mud samples were then rolled 16 hours at 250°F. After this time, the samples were screened through an 18-mesh sieve. The remaining Hole-Plug was washed, dried for four hours at 225°F and weighed. The % erosion losses were calculated assuming an initial moisture content of 8.8%.

Results

As described in Table 9, it can be seen that the addition of these acetylenic alcohols (Surfynol 502 and 504) to fresh water poly(vinyl alcohols) muds shows no improvement on shale stability. On the other hand, when Surfynol 504 is used in sea water muds there is an improvement on shale stability. In sea water, stable rheological and filtration control properties can be obtained with this polymer/surfactant system.

TABLE 9

Evaluation of Surfynol 502 and 504 on Poly(vinyl alcohol) Muds as Shale Stabilizers

Sample	40	41	42	43	44	45
Water, ml	300	300	300	300	300	300
Sea salt, g	-	-	-	13	13	13
Caustic, g	0.2	0.2	0.2	0.5	0.5	0.5
Airvol 540S, g	2	2	2	2	2	2
Milpac, LV, g	2	2	2	2	2	2
Biozan, g	0.7	0.7	0.7	0.7	0.7	0.7
Surfynol 502, ml	-	-	10	-	-	-
Surfynol 504, ml	-	-	10	-	-	10
Barite, g	204	204	204	204	204	204

Rheological Properties of Muds after Dynamic Aging at 250°F for 16 Hours

Sample	40	41	42	43	44	45
$\theta 600$	256	*	*	69	85	74
$\theta 300$	171	-	-	45	53	47
PV	85	-	-	24	32	27
YP	86	-	-	21	21	20
10-S	19	47	30	6	9	7
10-M	22	54	31	7	9	8
API, ml	8	4.8	6.0	10.4	6.0	6.0
% Erosion	91	87	93	17	17.5	12.7

* Off Scale

Examples 46-65

The following examples show the favorable use of water soluble polymers and surfactants comprised of sodium salts of naphthalene formaldehyde condensate.

Materials

The poly(vinyl pyrrolidone) used in these examples was Luviskol K-90 from BASF with MW=1,000,000 g/mol. The poly(vinyl alcohol) used was Airvol 540S with MW = 100,000 g/mol and a % hydrolysis of 88. The Arivol 540S was obtained from Air Products. Poly(vinyl pyrrolidone) and poly(vinyl alcohol) are referred to in this report as PVP and PVA, respectively. The surfactant used was Rhodacal N from Rhone-Poulenc. This surfactant is sold as a powder and it is the sodium salt of a sulfonated naphthalene-formaldehyde condensates. New Drill Plus from Baker Hughes Inteq was used for comparison studies. Hole-plug of 3/8" diameter was obtained from Baroid Corporation.

Equipment

Rheological properties were measured at room temperature in a 35 Fann Viscometer. The muds were mixed for 45 minutes in a multimixer. All erosion tests were done in steel cells and all solids contamination work was done in pint jars.

Samples

The erosion studies were done by placing the mud into steel cells with 25 grams of HOLE-PLUG. Then the cells were placed in an oven with rollers at the desired temperature for 20-16 hours. After this time, the cells were removed from the oven and allowed to cool to room temperature and the mud filtered through a mesh to isolate the intact HOLE-PLUG. The HOLE-PLUG was then washed with water and dried at 250°F for 4 hours prior to weighting. The % erosion is estimated

on basis of theses weights. The mud is then sheared and the rheological properties are measured.

Discussions

When Rhodacal N is added to a poly(vinyl pyrrolidone) sea water mud, it is observed that there is an improvement over the shale stability (Table 10, samples 46 and 47). In addition, there is no major change in the rheological properties of the mud even after heating to 250°F for 16 hours with constant movement. In a fresh water mud, the addition of this surfactant to PVP enhanced the shale stability considerably (93 Vs 34% without and with surfactant, respectively).

Table 11 illustrates the effect of Rhodacal N in poly(vinyl alcohol) muds. Addition of the surfactant to PVA reduces the % erosion to 12 after dynamic aging at 250°F for 16 hours. In a fresh water mud, no improvement is observed by adding the Rhodacal N. This system has good tolerance for solids as described in Table 13.

New Drill Plus (PHPA) was evaluated with this surfactant and the data is reported on Table 12. According to the results described on this Table, the addition of the Rhodacal N to New Drill Plus in fresh water muds reduces the percent erosion to 4% from 97%. Data on the effects of solids contamination (Table 14) shows that good filtration control is obtained with this system. However, other rheological properties change as the solids concentration increases.

TABLE 10

Evaluation of Rhodacal N with Poly(vinyl pyrrolidone) in Sea and Fresh Water Muds

Sample	46	47	48	59
Water, ml	300	300	300	300
Sea Salt, g	13	13	-	-
K-90, g	2	2	2	2
Caustic, g	0.5	0.5	0.2	0.2
Milpac LV, g	2	2	2	1
Biozan, g	0.75	0.75	0.75	0.3
Rhodacal, g	-	3.5	-	3.5
Barite, g	204	204	204	204

Rheological Properties of Muds after Dynamic Aging at 250°F for 16 Hours

Sample	46	47	48	49
θ600	66	66	172	78
θ300	44	42	114	46
PV	22	24	58	32
YP	22	18	56	14
API, ml	7.8	3	10	13
% Erosion	9	5	93	34

TABLE 11

Evaluation of Rhodacal N with Poly(vinyl alcohol) Muds in Sea and Fresh Water

Sample	50	51	52	53
Water, ml	300	300	300	300
Sea Salt, g	13	13	-	-
Arivol 540S, g	2	2	2	2
Caustic, g	0.5	0.5	0.2	0.2
Milpac LV, g	2	2	2	1
Biozan, g	0.75	0.75	0.75	0.3
Rhodacal, g	-	3.5	-	3.5
Barite, g	204	204	204	204

Rheological Properties of Muds after Dynamic Aging at 250°F for 16 Hours

Sample	50	51	52	53
$\theta 600$	49	64	184	238
$\theta 300$	33	44	125	178
PV	16	20	59	60
YP	17	24	66	118
API, ml	11	3	11	34
% Erosion	20	12.3	94	92

* Off Scale

TABLE 12

Evaluation of Rhodacal N with New Plus in Fresh Water

Sample	54	55
Water, ml	300	300
New Drill P, g	1	1
Caustic, g	0.2	0.2
Milpac LV, g	1	1
Rhodacal, g	3.5	-
Barite, g	204	204

Rheological Properties after Dynamic Aging at 250°F for 16 Hours

Sample	54	55
θ600	130	100
θ300	80	56
PV	50	44
YP	30	12
API, ml	5.4	6.5
% Erosion	4.4	97

TABLE 13

Effects of Solids Contamination on the Poly(vinyl alcohol)/Rhodacal N System in Sea Water

Sample	56	57	58	59	60
Water, ml	300	300	300	300	300
Sea Salt, g	13	13	13	13	13
Caustic, g	0.5	0.5	0.5	0.5	0.5
Arivol 540S, g	2	2	2	2	2
LD-8, g	0.05	0.05	0.05	0.05	0.05
Biolose, g	2	2	2	2	2
XC- Polymer, g	0.75	0.75	0.75	0.75	0.75
Rhodacal N, g	3.5	3.5	3.5	3.5	3.5
Barite, g	50	50	50	50	50
Rev-Dust, g	0	20	40	60	80

Rheological Properties after Dynamic Aging at 250°F for 16 Hours

Sample	56	57	58	59	60
θ600	38	39	43	52	60
θ300	25	25	30	36	42
PV	13	14	13	16	18
YP	12	11	17	20	24
10-S	3	3	6	7	6
10-M	2.5	3	6	8	7
API, ml	3.2	2.4	3.6	4.2	8.8
% Erosion	91	87	93	17	17.5

TABLE 14

Effects of Solids Contamination on the New Drill /Plus/Rhodacal N System in Sea Water

Sample	61	62	63	64	65
Water, ml	300	300	300	300	300
Sea Salt, g	13	13	13	13	13
Caustic, g	0.5	0.5	0.5	0.5	0.5
New Drill Plus, g	2	2	2	2	2
LD-8, g	0.05	0.05	0.05	0.05	0.05
Biolose, g	2	2	2	2	2
XC- Polymer, g	0.75	0.75	0.75	0.75	0.75
Rhodacal N, g	3.5	3.5	3.5	3.5	3.5
Barite, g	50	50	50	50	50
Rev-Dust, g	0	20	40	60	80

Rheological Properties after Dynamic Aging at 250°F for 16 Hours

Sample	61	62	63	64	65
θ600	58	69	86	100	130
θ300	41	49	64	76	96
PV	17	20	22	34	34
YP	24	29	42	42	62
10-S	4	6	8	11	14
10-M	3	6	8	11	16
API, ml	3	3	3	4	4

Examples 66 - 76

These examples show the synergistic effect of combining glycols with water soluble polymers and sulphosuccinate surfactants.

NEW DRILL PLUS and MILPAC, LV are Baker Hughes Inteq products. Aerosol IB-45 was obtained from American Cyanamide Corporation. Aerosol IB-45 is sold as a 50% solution in water. Aerosol IB-45 is sodium diisobutyl sulfosuccinate. Rhodacal N was obtained from Rhone Poulenc. Rhodacal N is a sodium salt of sulfonated naphthalene-formaldehyde condensate. Aerosol OS was obtained from American Cyanamid Corporation as a powder. Aerosol OS is sodium isopropylnaphthalene sulfonate. Glycols A-3192, A-3274, and AQUACOL D are Baker Hughes Inteq products. HOLE PLUG was obtained from Baroid Corporation and used as received.

Equipment

All laboratory barrels of fluid were mixed in a multimixer for a total of 45 minutes. The API's were measured in an API filtration apparatus. Rheological properties were measured at room temperature with a Fann 35 viscometer. Rolling erosion studies at 150°F were carried out in glass pint jars, and rolling erosion test performed at 250°F were carried out in steel cells.

Samples

Rolling erosion tests were performed by adding 25 grams of HOLE-PLUG (3/8" size) to each steel cell or glass jar containing the mud system prepared. Then, the cells were placed in an oven with rollers and allowed to roll at the desired temperature for 16 hours. After this time, the mud was filtered with a mesh and the non-reactive shale was then rinsed with water and dried at 250°F for four hours. The shale was finally weighted and the % erosion calculated. The properties of the muds

were then measured. The specific components, ratio of the components used to prepare the muds and the properties of the final samples after hot rolling are reported on Table 15.

Discussion

After evaluating several sulfosuccinate derivatives, the best performance (lowest % erosion) is obtained with Aerosol IB-45, which has the smallest substituent.

As described in Table 15, when IB-45 was added to a fresh water mud containing glycols, a slight negative effect on shale stability (samples 69 vs. samples 66 and 67) is observed. On the other hand, when Rhodacal N was used with a glycol like A-3192 and AQUACOLD improved shale stability was obtained. In a sea water environment, there is no negative effect and the % erosion was very low with both surfactants (IB-45 and Rhodacal N).

TABLE 15

Effects of Glycols on a Sulfosuccinate/Polymer Mud System

Sample	66	67	68	69	70	71	72	73	74	75	76
Water, ml	300	300	300	300	300	300	300	300	300	300	300
Sea Salt, g	-	-	-	-	-	-	13	13	13	13	13
Caustic, g	0.2	0.2	0.2	0.2	0.2	0.2	0.5	0.5	0.5	0.5	0.5
New Drill Plus, g	1	1	1	1	1	1	2	2	2	2	2
Milpac LV, g	2	2	2	2	2	2	2	2	2	2	2
Biozan, g	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
IB-45, ml	7	7	-	7	-	-	7	7	7	-	-
Rhodacal N, g	-	-	3.5	-	3.5	3.5	-	-	-	3.5	3.5
Barite, g	204	204	204	204	204	204	204	204	204	204	204
A-3192, ml	17.5	-	17.5	-	-	-	-	-	-	-	-
A-3274, ml	-	-	-	-	-	-	17.5	-	-	-	17.5
Aquacol D, ml	-	17.5	-	-	17.5	-	-	-	175.	-	-

Rheological Properties of Muds after Aging at 150°F for 16 Hours

Sample	66	67	68	69	70	71	72	73	74	75	76
$\theta 600$	145	230	168	222	195	222	170	174	168	177	212
$\theta 300$	84	163	120	158	138	155	116	124	116	127	137
PV	61	67	48	64	57	67	54	50	52	50	75
YP	23	96	72	94	81	88	62	74	64	77	52
10-S	11	22	18	24	20	27	13	15	12	18	15
10-M	14	24	19	26	22	28	13	14	12	18	15
API, ml	6.0	2.0	4.0	3.0	3.0	3.0	2.0	2.0	2.4	1.2	2.0
% Erosion	23	27	0	0	0	10	0	0	0	2	0

The foregoing examples thus demonstrate that sulphosuccinates and PHPA provide improved shale reduction results in fresh or salt (e.g., alkaline) water while suphosuccinates and PVA provide improvements in salt water only (as opposed to fresh water). Similarly, acetylenic alcohol surfactants and PVA provide improvement in salt water, but not in fresh water. The surfactants made from the sodium salts of sulfonated naphthalene-formaldehyde condensate provide improved shale reduction in fresh or salt water when combined with PHPA and PVP, but improvement is limited to salt water only (not fresh water) when combined with PVA.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

CLAIMS

CLAIM 1. An additive for aqueous well fluids comprising:

(a) at least one water soluble polymer; and

(b) a sulphosuccinate surfactant.

CLAIM 2. The well fluid additive of claim 1 wherein the water-soluble polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 3. The well fluid additive of claim 1 wherein the additive comprises in the range of about 0.1 to about 50 weight percent polymer and in the range of about 1 to about 50 weight percent sulphosuccinate surfactant.

CLAIM 4. The well fluid additive of claims including:

at least one glycol.

CLAIM 5. A well fluid comprising:

(a) an aqueous component;

(b) at least one water soluble polymer; and

(c) a sulphosuccinate surfactant.

CLAIM 6. The fluid of claim 5 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides,

and partially hydrolyzed polyacrylamides.

CLAIM 7. The fluid of claim 5 including:

at least one glycol.

CLAIM 8. The fluid of claim 5 wherein said aqueous component comprises fresh water and said polymer comprises partially hydrolyzed polyacrylamide.

CLAIM 9. The fluid of claim 5 wherein said aqueous component comprises salt water and said polymer comprises partially hydrolyzed polyacrylamide or polyvinylalcohol.

CLAIM 10. A method of stabilizing a subterranean formation penetrated by a borehole and wherein the formation comprises water-sensitive materials, the method comprising introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid comprises at least one water-soluble polymer and a sulphosuccinate surfactant.

CLAIM 11 The method of claim 10 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 12. The method of claim 10 including:

adding at least one glycol to the formation treatment fluid.

CLAIM 13. The method of claim 10 wherein said aqueous component comprises fresh water and said polymer comprises partially hydrolyzed polyacrylamide.

CLAIM 14. The method of claim 10 wherein said aqueous component comprises salt water and said polymer comprises partially hydrolyzed polyacrylamide or polyvinylalcohol.

CLAIM 15. An additive for aqueous well fluids comprising:

(a) at least one polymer; and

(b) an acetylenic alcohol surfactant.

CLAIM 16. The well fluid additive of claim 15 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 17. The well fluid additive of claim 15 including:

at least one glycol.

CLAIM 18. The well fluid additive of claim 15 wherein the additive comprises in the range of about 0.1 to about 50 weight percent polymer and in the range of about 1 to about 50 weight percent acetylenic alcohol surfactant.

CLAIM 19. A well fluid comprising:

(a) an aqueous component;

(b) at least one water soluble polymer; and

(c) an acetylenic alcohol surfactant.

CLAIM 20. The fluid of claim 19 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamide.

CLAIM 21. The fluid of claim 19 including:

at least one glycol.

CLAIM 22. The fluid of claim 19 wherein said aqueous component comprises salt water and said polymer comprises polyvinyl alcohol.

CLAIM 23. A method of stabilizing a subterranean formation penetrated by a borehole and wherein the formation comprises water-sensitive materials, the method comprising introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid comprises at least one water soluble polymer and an acetylenic alcohol.

CLAIM 24. The method of claim 23 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 25. The method of claim 23 including:

adding at least one glycol to the formation treatment fluid.

CLAIM 26. The method of claim 23 wherein said aqueous component comprises salt water and said polymer comprises polyvinyl alcohol.

CLAIM 27. An additive for aqueous well fluids comprising:

(a) at least one water soluble polymer;

(b) a surfactant comprises of at least one sodium salt of sulfonated napthlene formaldehyde condensate.

CLAIM 28. The well fluid additive of claim 27 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 29. The well fluid additive of claim 27 wherein the additive comprises in the range of about 0.1 to about 50 weight percent polymer and in the range of about 1 to about 50 weight percent of said surfactant.

CLAIM 30. The well fluid additive of claim 27 including:

at least one glycol.

CLAIM 31. A well fluid comprising:

(a) an aqueous component;

(b) at least one water-soluble polymer; and

(c) a surfactant comprised of at least one sodium salt of sulfonated naphthalene formaldehyde condensate.

CLAIM 32. The fluid of claim 31 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylpyrrolidone copolymers, polyvinylalcohol, starches, cellulosic derivatives, polyanionic cellulose, polysaccharides, and partially hydrolyzed polyacrylamides.

CLAIM 33. The fluid of claim 31 including:

at least one glycol.

CLAIM 34. The fluid of claim 31 wherein said aqueous component comprises salt water and said polymer comprises partially hydrolyzed polyacrylamide, polyvinylpyrrolidone or polyvinylalcohol.

CLAIM 35. The fluid of claim 31 wherein said aqueous component comprises fresh water and said polymer comprises partially hydrolyzed polyacrylamide or polyvinylpyrrolidone.

CLAIM 36. A method of stabilizing a subterranean formation penetrated by a borehole and wherein the formation comprises water sensitive materials, the method comprising introducing a formation treatment fluid into the borehole and into contact with the formation, wherein the formation treatment fluid comprises at least one water soluble polymer and a surfactant comprised of at least one sodium salt of

sulfonated naphthalene formaldehyde condensate.

CLAIM 37. The method of claim 36 wherein the polymer is selected from the group of polymers consisting of polyvinylpyrrolidone, polyvinylalcohol and partially hydrolyzed polyacrylamide.

CLAIM 38. The method of claim 36 including:

adding at least one glycol to the formation treatment fluid.

CLAIM 39. The method of claim 36 wherein said aqueous component comprises salt water and said polymer comprises partially hydrolyzed polyacrylamide, polyvinylpyrrolidone or polyvinylalcohol.

CLAIM 40. The method of claim 36 wherein said aqueous component comprises fresh water and said polymer comprises partially hydrolyzed polyacrylamide or polyvinylpyrrolidone.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 95/10022

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09K7/02 B01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP,A,0 673 984 (M-I DRILLING FLUIDS) 27 September 1995 see page 3, line 28 - page 4, line 6 see page 4, line 45 - line 51 ---	1-3,5,6
X	US,A,4 433 731 (J,CHATTERJI) 28 February 1984 see column 3, line 37 - column 4, line 51 see claims 1,2; example 3 ---	27-29, 31,32, 34,36
Y	GB,A,2 086 923 (NL INDUSTRIES) 19 May 1982 see page 1, line 27 - line 52 see page 2, line 5 - line 39 ---	1,4
Y	FR,A,2 624 132 (BAKER HUGHES) 9 June 1989 see page 2, line 19 - page 5, line 16 see page 6, line 4 - page 7, line 33 --- -/--	1,4

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
22 December 1995	15.01.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Boulon, A

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/10022

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 112 836 (HALLIBURTON) 27 July 1983 see page 2, line 3 - line 17 see claims 1-14 -----	15,19

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